Unexpected CFC-11 Emissions: the Ramifications for CTC

CTC: An update on its Production

How much is available?

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Unexpected CFC-11 Emissions: the Ramifications for CTC

• CFC-11 is made by the reaction of AHF and CTC

• CFC-11 usually co-produces an amount of CFC-12*, maybe 15-30%

• When we can estimate the actual production of CFC-11, we will know how much CTC is required: at best we expect +/- 1.18 units of CTC

• CTC used to make CFC-11/12 is a feedstock use and therefore is non-controlled; there will be fugitive losses

• This presentation is about how CTC is made, and where it is to be found, in and what quantity
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- The annual quantities of CFC-11/-12 being produced are likely to be between 10ktpa (100% CFC emitted) and 60kt (20% emitted, balance retained)

- We do not yet know how much CFC-12* has been co-produced. We assumed 0%, 15%, and 30%. We don’t know how it was used, or if it was

- The range of CTC required lies between 12kt to 20kt in the low range, and 70-100,000kt in the worst case

*Important not just as an ODS but has a potent high-GWP, of 10,900
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How is CTC made?

• CTC is made today by two processes: on chloromethanes (CMs) plants and on Perchloroethylene/CTC plants (PCE/CTC plants)

• On CM plants, CTC is an inevitable part of the chlorination process. Demand decline → minimising CTC production, usually seen as 5% of total CMs, but flexible to make more if required.

• PCE/CTC plants were initially built to feed demand to CFCs at maybe 5:95 ratio of PCE/CTC. Like CM plants, minimisation led to 85:15 PCE:CTC ratios. Investment of $10-20m necessary to upgrade to 100% PCE; many exited. Flexible back to 95% CTC if needed.
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CTC from “Higher” Chloromethanes

- There are 52 chloromethane producers globally, many having two or more locations.

- *Installed CM capacity is 4 million tons. 70% of the capacity is in Art. 5 countries*

- Chloromethanes are made by reacting methyl chloride with chlorine: co-production of methylene chloride, chloroform and CTC is inevitable

- *CTC has been minimised because supply >demand. Excepting China, a good global average is 5% on DCM/CFM. Some Chinese plants maintain that 3% is the norm on new equipment, although it seems low*

- Some producers have higher ratios and some produce CTC deliberately for intermediate. CM producers agree that up to 15% CTC on “highers” is possible without disruption.
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Why is CTC made?

- Fluorocarbons: new generation fluoro-propanes and butanes such as HFC236fa, HFC245fa and HFC365mfc require the reaction of CTC with an olefin (ethylene, perchloroethylene). Some HFOs use a similar reaction, but there are (more expensive) alternatives based on HCFC-22 (India, China, Japan)

- DV Acid Chloride uses CTC as feedstock in its early stages of manufacture (India, China)

- “Crude” CTC from CM plants can be fed to PCE/CTC plants to make either PCE or feedstock-grade CTC (US, EU)

- Some CTC is dehydrochlorinated back to CFM, DCM or methyl chloride, which can produce more chloromethanes or be diverted to silicone production, where it is vital to the production chain (China, Japan)

- In China, fluorocarbon-grade PCE is made by the reaction of CTC with methane and chlorine. Six such plants have been notified, two more coming
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.....or failing this, must be destroyed, which is a cost

Total CTC destruction reported by Parties  
(in metric tonnes)

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CTC from Higher Chloromethanes

*One way to look at CTC from CMs is by capacity utilisation (2018 figures)*

<table>
<thead>
<tr>
<th>Region</th>
<th>Capacity</th>
<th>Available CTC from CMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe</td>
<td>&lt;500</td>
<td>5-10</td>
</tr>
<tr>
<td>Russia</td>
<td>&lt;100</td>
<td>?5</td>
</tr>
<tr>
<td>USA</td>
<td>&lt;500</td>
<td>10</td>
</tr>
<tr>
<td>China</td>
<td>&gt;2500</td>
<td>125-250</td>
</tr>
<tr>
<td>Japan</td>
<td>&lt;250</td>
<td>5-10</td>
</tr>
<tr>
<td>India</td>
<td>&lt;250</td>
<td>0</td>
</tr>
<tr>
<td>Other Asia</td>
<td>&lt;100</td>
<td>(-10)</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>4000</td>
<td></td>
</tr>
<tr>
<td><strong>Utilisation</strong></td>
<td>70-75%</td>
<td></td>
</tr>
</tbody>
</table>

These tables demonstrate that by today’s look, some regions would have capacity to supply 10-20ktpa but few have enough capacity to cover the amount of CTC at the higher end of estimated CTC feedstock for the unaccounted CFC-11
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CTC from Higher Chloromethanes

Let's step back to 2013......

Global CTC Potential, ktpa
minimum and maximum

<table>
<thead>
<tr>
<th>Capacity</th>
<th>At 5% CTC</th>
<th>At 15% CTC</th>
</tr>
</thead>
<tbody>
<tr>
<td>3650</td>
<td>180</td>
<td>550</td>
</tr>
<tr>
<td><strong>Actual</strong></td>
<td><strong>2700-2900</strong></td>
<td><strong>420</strong></td>
</tr>
</tbody>
</table>

Global Capacity, CMs, 2013 (ktpa)

<table>
<thead>
<tr>
<th>Region</th>
<th>Capacity</th>
<th>Capacity to supply CTC from CMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe</td>
<td>&lt;800</td>
<td>30-705</td>
</tr>
<tr>
<td>Russia</td>
<td>&lt;100</td>
<td>5</td>
</tr>
<tr>
<td>USA</td>
<td>&lt;500</td>
<td>10-20</td>
</tr>
<tr>
<td>China</td>
<td>&lt;1800</td>
<td>150-300</td>
</tr>
<tr>
<td>Japan</td>
<td>&lt;250</td>
<td>5-10</td>
</tr>
<tr>
<td>India</td>
<td>&lt;210</td>
<td>0</td>
</tr>
<tr>
<td>Other Asia</td>
<td>&lt;100</td>
<td>5-10</td>
</tr>
<tr>
<td>TOTAL</td>
<td>3365060-370</td>
<td></td>
</tr>
</tbody>
</table>

It is not clear from the total that CFM declined (phase-down emissive HCFC-22) whilst DCM increased (HFC-32). Some areas could have capacity for the low-end (10kt) of our CTC range, but few would have more than 20ktpa available.

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CTC from PCE/CTC plants

- High temperature reaction of C₁-C₃ chlorinated waste streams (from VCM/EDC plants, from CH-PO plants, and incl “crude” CTC from CMs) with chlorine to make pure PCE and CTC streams.

- Mainly made for CFC boom: bias to CTC, some PCE to CFC₁₁₃, some to solvent. CTC was once >1 million tpa. First plants could work 10:90 PCE/CTC to 80:20 PCE/CTC

- Investment to 100% PCE cycle about $10m-$20m. Many Plants closed.

- Global capacity for PCE/CTC is <360 ktpa (5 plants, USA/EU only). Deliberate production CTC ≥80kt and increasing. Spare capacity in Europe, none in USA. This is “made on Demand CTC”. But is it likely......?
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Summing it all up...

CTC from Chloromethanes
- Inevitable, but can be minimised to 5%. Ground zero is 140kt
- More can be made by ratio management
- Some areas could produce enough for low-end need 12-20kt, few could deliver 40-100kt

CTC from PCE/CTC plants
- Can produce 0-100% CTC, CTC is made to demand
- Spare capacity to produce, after existing PCE and CTC commitments are met
Estimated emissions ~ 10

D. Legacy

A. Unreported inadvertent

Total inventory of emissions = 15

B. Unreported non-feedstock

(i) incineration

(ii) PCE production

(iii) HFC production

(iv) MeCl production

(v) DVAC production

(vi) process agent

Total CTC production = 203

chlorine production & usage

industrial and domestic uses of chlorine

e.g. paper bleaching, disinfection

Chlorine

chlor-alkali plants

historic landfill & contaminated soil

PCE/CTC plants

chloromethanes plants

feedstock usage

0.2

0.2

0.2

1.1

0.3
### Estimated CTC Consumption by application 2018

<table>
<thead>
<tr>
<th>Region</th>
<th>Use in HFC/HFO</th>
<th>Use in PCE/CTC</th>
<th>CTC→PCE</th>
<th>Use in DVAC</th>
<th>Dechlorination to CFM, DCM and MeCl</th>
<th>Destruction or not-known</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe</td>
<td>16.0</td>
<td>20.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8.0</td>
<td>44.0</td>
</tr>
<tr>
<td>Russia</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>NAFTA</td>
<td>69.0</td>
<td>21.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>90.0</td>
</tr>
<tr>
<td>China</td>
<td>24.0</td>
<td>0</td>
<td>60.0</td>
<td>4.0</td>
<td>30.0</td>
<td>5.0</td>
<td>123.0</td>
</tr>
<tr>
<td>India</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>20.0</td>
<td>0</td>
<td>0</td>
<td>20.0</td>
</tr>
<tr>
<td>Japan</td>
<td>14.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14.0</td>
</tr>
<tr>
<td>S Korea</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>123</td>
<td>41</td>
<td>60</td>
<td>24</td>
<td>26</td>
<td>18.0</td>
<td>296</td>
</tr>
</tbody>
</table>

*Approx. 33% PCE/CTC, 67% CMs*
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Thank you for your kind attention

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Kharasch reactions are vital to CTC intermediate use

- \[ \text{CH}_2=\text{CH}_2 + \text{CTC} = \text{CH}_2\text{Cl}-\text{CH}_2-\text{CCl}_3 \text{ (HCC250fb: starter to HFO1234yf)} \]

- \[ \text{CH}_2=\text{CHCl} + \text{CTC} = \text{CHCl}_2-\text{CH}_2-\text{CCl}_3 \text{ (HCC240fa: starter for HFC245fa, HFCO1233xd, HFO1234ze)} \]

- \[ \text{CH}_2=\text{CH-CN}_3 + \text{CTC} = \text{tetrachlorobutyronitrile (starter to DVAC synthetic pyrethroid)} \]

- \[ \text{And... CTC} + 2\text{Cl}_2 + \text{CH}_4 = \text{CCl}_2=\text{CCl}_2 \text{ (PCE + 4HCl)} \]